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NL-3130 AC Vlaardingen(NL)(54) **Liquid detergent compositions.**

(57) An aqueous thixotropic automatic dishwashing composition comprises a chlorine bleach, a cross-linked polymeric polycarboxylate thickener of high molecular weight, a soluble detergency builder of which at least part is a polymeric polycarboxylate builder of relatively low molecular weight, and an alkaline buffer system comprising an alkali metal silicate and an alkali metal hydroxide which provides a high pH. The compositions may be formulated to be translucent and to have a long gel life.

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Background of the Invention

The invention relates to liquid detergent compositions which are suitable for automatic dishwashing. Such products are increasing in popularity because of their convenience compared to conventional powdered detergent products. In particular, the liquids are easier to dose into dispensing devices in automatic dishwashing machines, and do not cake as powders may do when stored in conditions of high temperature and humidity.

However, liquid automatic dishwashing compositions are themselves subject to certain problems. Fluid components of low viscosity cannot readily be dosed into automatic dishwashing machines using conventional dosing devices from which they tend to leak prematurely. More concentrated compositions of higher viscosity which contain suspended solid materials can be better for such dosing because of the structuring effect of the insoluble particles, but can be subject to phase separation, or syneresis, on standing over a period of time, particularly if subjected to elevated temperatures. This results in a caked layer of moist solids with a supernatant liquid, which is immediately apparent to the consumer when the product is used, besides giving inferior washing performance.

One difficulty in formulating stable liquid detergent compositions for automatic dishwashing is the desired presence of a chlorine-releasing bleaching agent. Such materials are conventionally present in nearly all commercially-successful automatic dishwashing products because of the beneficial effect on the cleaning performance, especially stain removal, and their useful disinfectant effect. However, the chlorine-releasing bleaching agents which are used have a major disadvantage in that the chlorine tends to react with the ingredients of the composition itself, sometimes to harmful effect. Although this is not a significant problem in powdered detergent compositions, it is particularly damaging in liquid detergent compositions in which the chlorine-releasing bleaching agent and the other ingredients are in much more intimate contact. This tends to limit the effective shelf life of commercial products.

Liquid automatic dishwashing compositions have commonly incorporated both inorganic thickening agents such as clays, and inorganic detergency builders, because such materials are resistant to attack by chlorine. But the clays are insoluble materials and the phosphate builders can be present in partially insoluble form if used in an amount sufficient for full building in hard water areas, which can contribute to syneresis for such compositions. Moreover such compositions containing appreciable amounts of insoluble ingredients are necessarily opaque, and there is a perceived consumer demand for translucent compositions, which are thought to be more pure.

The Prior Art

Many attempts have been made to formulate liquid detergent compositions for automatic dishwashing which are thixotropic liquids containing chlorine bleaching agents and which are fully stable during storage for long periods under domestic conditions. Although the patent literature is replete with descriptions claiming to have been successful in this respect, in practice the perfectly stable composition has yet to be made. Proposals have also been made for translucent compositions, but without as yet achieving fully satisfactory properties in other respects. Examination of the commercially available products shows there is still scope for improvement in this respect.

Many proposals for thickening liquid detergent compositions for dishwashing purposes have involved the use of clays, as described for example in U.S. Patent 4,116,849 (Leikhim), U.S. Patent 4,431,559 (Ulrich), U.S. Patent 4,740,327 (Julemont et al.), U.S. Patent 4,511,487 (Pruhs et al.), U.S. Patent 4,512,908 (Heile) and U.S. Patent 3,558,496 (Zmoda).

It has also been suggested to use clay thickening agents together with other materials to inhibit phase separation or change the viscosity characteristics. For example U.S. Patent 4,752,409 (Drapier) mentions the use of polyvalent metal salts of long-chain fatty acids in clay thickened compositions. European Patent application 345,611A (Delvaux) also recommends the use of metal salts of fatty acids in clay thickened compositions having a pH of at least 11.2. In U.S. Patent 4,857,226 (Drapier) the combination of polyacrylate and a polyvalent metal salt of a fatty acid is recommended to improve the stability of phosphate built compositions with clay thickening agents. European patent application 264,975A (Fuchs) recommends high levels of SiO₂ to improve the stability of clay-thickened compositions. In U.S. Patent 4,927,555 (Colarusso), special processing is used for clay-thickened products.

There have also been some proposals for avoiding the use of clay thickeners, such as G.B. patent application 2,185,037A (Dixit) which uses an amount of aliphatic carboxylic acid, and U.S. Patent 4,147,650 (Sabatelli) using a concentrated alkaline slurry system.

The use of polymers for thickening liquid detergent compositions has been disclosed in many patents

including U.S. Patent 3,060,124 (Ginn), U.S. Patent 4,226,736 (Bush), U.S. Patent 4,228,048 (Tesdaahl), and G.B. patent application 2,219,596A (Prince), sometimes in combination with a clay, as for example in G.B. Patent 2,164,350B (Lai et al), U.S. Patent 4,857,226 (Drapier) and U.S. Patent 4,867,896 (Elliott).

Recently, in U.S. Patent 4,836,948 (Corring) it is suggested to use a cross-linked polycarboxylic acid polymer and a small amount of a co-structurant such as alumina in liquid dishwashing compositions in gel form, which have viscoelastic properties to facilitate dosing of the compositions without dripping, and the compositions can be translucent or transparent. U. S. Patent 4,859,358 (Gabriel) discloses aqueous phosphate built dishwashing compositions with clay or polymeric polycarboxylate thickening agents and containing long chain hydroxy fatty acids to inhibit silverware tarnishing. In U.S. Patent 4,933,101 (Cilley), the use of insoluble zinc compounds is suggested to inhibit glassware corrosion in similar compositions, which can be translucent.

Summary of the Invention

It is an object of the present invention to provide aqueous thixotropic liquid detergent compositions suitable for automatic dishwashing which have improved stability despite the presence of chlorine bleach.

The present invention provides an aqueous thixotropic liquid detergent composition suitable for automatic dishwashing having improved stability which comprises:

- a. about 0.1 to 5% of a chlorine-releasing bleach agent (calculated as available chlorine),
 - b. about 0.1 to 5% of a cross-linked polycarboxylate thickening agent derived from an unsaturated mono or di-carboxylic acid of 3 to 6 carbon atoms having a molecular weight of at least 1,000,000 and cross-linked by at least about 0.75% of a cross-linking agent based on the monomeric constituents,
 - c. about 1 to 30% of a detergency builder of which at least about 0.25% is an alkali metal or ammonium polymeric polycarboxylate having a molecular weight of from about 1,000 to 100,000,
 - d. about 1 to 30% of an alkaline buffer system comprising an alkali-metal silicate, or an alkali-metal hydroxide or a mixture thereof, sufficient to provide a pH of from about 12 to 13.5,
- wherein all percentages are by weight of the composition.

It has been found that compositions having these essential requirements can be formulated having excellent cleaning performance and improved shelf-life, with either a wholly non-phosphate or a low-phosphate builder systems and optionally being translucent in nature. Because of the high viscosity, except when subject to shear, the compositions are commonly called gels, but are more correctly described as thixotropic liquid products. Preferably the compositions have a viscosity of about 1,000 to 20,000 centipoises (cps) more preferably about 1,500 to 10,000 cps at 25°C under minimum shear conditions of 5 sec⁻¹. Under flow conditions represented by 25 sec⁻¹, the viscosity is preferably about 200 to 5,000 cps, optimally about 400 to 2,500 cps. Viscosity is measured using a Haake Rotovisco RV - 100 Viscometer. The viscosity of the compositions may increase substantially on standing for a period after manufacture, before then decreasing gradually during storage until the product is used by the consumer.

The compositions of the invention can be formulated to have an effective gel life of at least 20 days at 50°C, which in practical terms is equivalent to a shelf life of at least 6 months at ambient temperature, and the preferred compositions may be prepared with a shelf life in excess of 1 year at room temperature, which represents a substantial improvement on the commercially available liquid detergent compositions for automatic dishwashing provided for the public hitherto.

In accordance with the invention the improved stability for the compositions is achieved by using in combination a specific cross-linked polycarboxylate thickening agent which has good resistance to chlorine bleach, a polymeric polycarboxylic builder also resistant to chlorine, and an alkaline buffer system with an alkali metal silicate of specified type and/or an amount of alkali metal hydroxide to provide a high pH, all of which combine in a synergistic manner in the presence of a chlorine releasing bleach agent to provide the improved properties which are desired.

The compositions may also be translucent, by which it is meant that at least about 5% of light is transmitted through a 2 cm sample of a composition. In one embodiment, the compositions are effectively transparent or clear, by which it is meant that they transmit at least about 10% of light, preferably at least about 20% of light, through such a sample.

Detailed Description of the Invention

An essential ingredient in the automatic dishwashing compositions is a chlorine bleaching agent, which is commonly sodium hypochlorite, because it is readily available and inexpensive. Other chlorine releasing bleaching agents may be used if desired, for example potassium and calcium hypochlorite, tetracyclic N-

bromo and N-chloroimides such as trichlorocyanuric, tribromocyanuric, dibromo and dichloro cyanuric acids and salts thereof, especially the sodium and potassium salts. An example of a hydrated dichlorocyanuric acid is Clearon CDB56, manufactured by Olin Corporation. The chlorine-releasing bleaching agent is normally present in the compositions at a level to provide from about 0.1 to 1.5% available chlorine during use. Preferred compositions will produce about 0.5 to 1.2% available chlorine.

The detergent compositions of the invention also include a detergency builder which functions to sequester hardness ions, i.e., calcium and magnesium present in the wash water. If these cations are not sequestered, they can form undesirable precipitates and cause unsatisfactory cleaning properties, often with spotting or filming on the articles being washed.

The detergency builder compounds should be chlorine-resistant and are preferably soluble. A polymeric polycarboxylate compound can be used alone or in a mixture of such a compound with another detergency builder, for example a phosphate compound. The polymeric polycarboxylates of relatively low molecular weight in the ranges of about 1,000 to 100,000 have been found to be effective detergency builders, whilst also contributing to product stability, especially in the absence of phosphate co-builders. This is particularly advantageous for countries or regions where legislation prohibits phosphate-based products to be used because of the possible contribution to eutrophication in ground waters.

Suitable polymeric polycarboxylic compounds include the homopolymers of acrylic acid, methacrylic acid, maleic acid, itaconic acid and the like, as well as copolymers of such materials and their alkali metal salts, optionally with an amount of a non-carboxylate compound such as vinyl methyl ether or styrene. Examples of commercially available non-phosphate builder compounds include Alcosperse 602-N from Alco Chemical Company (MW 4,500), Acrysol LMW-20N (4,500) from Rohm & Haas, and Sokalan PA-30 (8,000) from BASF. The amount of the polymeric polycarboxylate compound is normally from about 0.25 to 15%, preferably not more than about 5%, by weight of the composition.

Mixtures of the polymeric polycarboxylate builders with other soluble builder compounds may advantageously be used. These can have the advantage of being cheaper than the wholly polymeric polycarboxylate products while achieving good detergency in hard water areas.

Phosphate detergency builders which can be used include particularly the pyrophosphates and polyphosphates, as well as organophosphates, usually in the form of the alkali metal, ammonium or substitute ammonium salts. Preferred phosphate builders are sodium and potassium tripolyphosphate salts, which have good detergency building properties, but the pyrophosphates can be useful because of the better solubility characteristics. A mixture of sodium tripolyphosphate and potassium pyrophosphate has been found to be particularly effective in providing good detergency building whilst being sufficiently soluble so that the detergent compositions can be translucent. Moreover, it has been found that the combination of the polymeric polycarboxylate with sodium tripolyphosphate appears to enhance the solubility of the latter so as to facilitate the formulation of translucent compositions with sufficiently high builder levels. When such phosphate builder salts are used, the amount is preferably from about 3 to 20% by weight of the compositions, in addition to the amount of polymeric polycarboxylate builder.

Additionally, other soluble non-phosphate detergency builder compounds may be present, which may be inorganic, for example the alkali metal carbonates, bicarbonates, sesquicarbonates, which also provide useful buffering capacity, or zeolites. Example of other organic non-phosphate builder compounds are alkali metal salts of nitrilotriacetic, oxydisuccinic, oxydiacetic, carboxymethyl oxysuccinic, and citric acids.

An essential ingredient in the liquid detergent compositions of the invention is a polycarboxylate thickening agent, which is derived from an unsaturated mono or di-carboxylic acid having 3 to 6 carbon atoms and a relatively high molecular weight of at least 1,000,000, and which is cross-linked by at least about 0.75%, preferably greater than about 1%, of a cross-linking agent based on the monomeric constituents. Examples of suitable unsaturated acids are acrylic, methacrylic, maleic, fumaric, itaconic, citraconic, and mesaconic acids. In addition to the primary monomers, there may be at least one secondary monomer or comonomer, for example an acrylic or methacrylic acid ester with a C₁-C₂₀ alkyl group, such as methyl acrylate, ethyl acrylate or propyl acrylate or a corresponding methacrylate. Further useful secondary monomers include acrylonitrile, acrylamide, alpha-olefins such as ethylene and propylene, vinyl chloride and vinyl methyl ether. If any such comonomer is used it is preferably less than about 10% by weight of the primary monomer.

The polymeric thickening agents are required to be cross-linked with a di- or polyunsaturated compound, for example a polyalkenyl polyether such as allyl sucrose, or allyl pentaerythritol, diallyl maleate, ethylene glycol dimethacrylate, diolefins such as 1,5-hexadiene, butadiene and isoprene, and polyalkenyl cyclic compounds such as trivinylcyclohexane and divinyl benzene. The most preferred cross-linked polycarboxylate thickening agents are derived from acrylic acid or its salts which are cross-linked with allyl sucrose, allyl pentaerythritol or 1,2,4-trivinylcyclohexane.

Polymeric polycarboxylate thickening agents are further described in U.S. Patents 2,798,053 (Brown), U.S. Patent 2,810,716 (Markus), U.S. Patent 2,985,625 (Jones), U.S. Patent 4,228,048 (Tesdaal), U.S. Patent 4,130,501 (Lutz et al.), and in U.S. Patent 4,867,896 (Elliott et al.), which are hereby incorporated by reference.

5 The polycarboxylate thickening agents are required to have a molecular weight of at least 1,000,000. The molecular weights can be up to about 25,000,000 and preferably up to about, for example, from about 1,000,000 to 10,000,000. The amount of cross-linking depends on the nature of the cross-linking agent present, but is normally within the range of about 0.75 to 6% based on the monomeric constituents. It can be at a lower level within this range for cross-linking agents having 3 or more unsaturated groups, but is preferably at a higher level within this range where there are only 2 unsaturated groups present in the cross-linking agent. More specifically, the preferred level of cross-linking is about 2 to 6% for 2 unsaturated groups, about 1 to 4% for 3 unsaturated groups, and about 1 to 2.5% for 4 or more unsaturated groups per monomer unit, calculated by weight of total unsaturated carboxylic acid and comonomer content.

10 Examples of commercially available cross-linked polymeric polycarboxylated thickening agents which are based on polyacrylic acid cross-linked with polyalkenyl polyethers, are the Carbopol resins manufactured by B. F. Goodrich Chemical Co., for example the materials known as Carbopol 934 (MW 3 million) Carbopol 940 (MW 4 million), Carbopol 617 or 627 (MW 4 million). Especially preferred are the types which do not contain benzene, for example Carbopol 627.

15 The polymeric thickening agent should be used in the compositions of the invention in an amount from about 0.1 to 5% by weight of the composition, preferably in an amount from about 0.1 to 3%, especially about 0.25 to 2.5% by weight of the composition.

20 There is no need to incorporate a clay thickening agent in the compositions of the invention as commonly utilized in commercial liquid dishwashing compositions hitherto, and preferably the compositions are substantially free of such materials. Clays have the disadvantage when used as the main thickening agent that they tend to interact with some ingredients in detergent compositions, with the result that the viscosity of the compositions changes over time and syneresis can result from this. The presence of substantial amounts of clay also prevents the formulation of detergent compositions which are translucent.

25 However, it is possible to include in the detergent compositions a small amount of clay as an auxiliary thickening agent if desired. Suitable clays for this purpose include the classes of smectites, kaolins, illites, chlorites and attapulgites. Specific examples of such clays include bentonite, pyrophyllite, hectorite, saponite, sauconite, nontronite, talc and beidellite as types of smectites. Less preferable are illites such as bravaisite, muscovite, paragonite and phlogopite, chlorites such as corrensite, penninite, donbassite and sudoite, or attapulgites such as sepiolite and polygorskite.

30 Examples of commercial hectorites which can be used are the Laponites from Laporte Industries, Veegum Pro and Veegum F from R. T. Vanderbilt, USA, and Barasymms, Macaloids and Propaloids from Baroid Division of National Lead Company, USA. Particularly preferred are the synthetic hectorites Laponite S, Laponite RD, Laponite RDS and Laponite XLS.

35 Further auxiliary thickening agents which may advantageously be used in conjunction with polymeric thickening agents are disclosed in European Patent application 323,209A (Corring), which is hereby incorporated by reference.

40 The amount of any such clay auxiliary thickening agent which can be used is from about 0.01 to about 2% by weight, preferably from not more than about 0.5% by weight of the compositions.

45 Another type of additive which can be used to increase viscosity and/or gel life is a fatty acid salt with a multi-valent cation, for example aluminum or zinc stearate. The use of such fatty acid salts in conjunction with clay thickening agents is described in U.S. Patent 4,752,409 (Drapier). We have found zinc stearate to be useful, and even at low levels between 0.2 and 0.4% by weight there can be a marked increase in viscosity and increased gel life on storage at high temperatures. But such additives are preferably used at levels which retain the translucency of the compositions.

50 It is required that the compositions of the invention should contain an alkaline buffer system to provide a pH of at least about 12 but not more than about 13.5. Surprisingly, it was found that a higher pH within this range in combination with high crosslink density contributes to product stability in a synergistic fashion, compared with using a conventional pH in the range of about 11 to 12 for other liquid detergent compositions. Preferably the pH is from about 12.3 to about 13, since compositions of pH much higher than this can become hazardous during domestic use and require warning labels. In order to achieve the high pH it is necessary to have present an alkali metal hydroxide especially sodium or potassium hydroxide, normally in an amount of 0.1 to about 3% by weight of the composition, and preferably 1.0 to 2.5%, or higher amounts of a suitable alkali metal silicate such as metasilicate, according to the desired pH for the product.

The presence of an alkali metal silicate is also beneficial for reducing corrosion and alkaline attack on glass during dishwashing at high pH. Alkali metal silicate of $\text{SiO}_2:\text{Na}_2\text{O}$ ratio about 1 to 3 may be used. However, it has been found that sodium silicate having a ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of about 1.6 to 2.2 is particularly advantageous for the stability of the compositions of the invention. Preferably sodium silicate is used with a ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of about 2.0, for example the material available commercially as Britesil H20 from PQ Corporation. Potassium silicate can be employed if desired but is more expensive.

The amount of the alkali metal silicate used is preferably from about 2 to 20%, more preferably from about 3 to 15% by weight of the composition. Mixtures of different alkali metal silicates, for example sodium silicate of ratio 2 with sodium metasilicate or sodium RS silicate, may be used if desired.

The compositions of the invention should have low foaming properties for use in automatic dishwashing machines, but may contain a surfactant if desired to improve performance and also to act as a rinse aid. Preferably the surfactants are resistant to chlorine bleach. Nonionic surfactants are particularly desirable, for example compounds of the polyoxyalkylene type as described in U.S. Patent 4,836,948 (Corring), and U.S. Patent 4,877,544 (Gabriel) which are hereby incorporated by reference. Anionic surfactants may also be used, particularly those which are more resistant to attack by chlorine such as alkyl diphenyl oxide sulphonate, alkyl naphthalene sulphonate, or sodium 2-acetamidohexadecane sulphonate.

The amount of such surfactant if used is generally from about 0.1 to 10%, preferably from about 0.2 to 5%, and most preferably from 0.2 to 3% by weight of the composition.

Additionally, defoaming agents may be employed if desired, for example alkyl phosphates, certain hydrocarbon waxes, hydrophobic silicas, silicone defoamers or certain alkyl carboxylates and the like. The preferred defoaming agents are the alkyl phosphates and silicone defoamers, which have a lower tendency to deposit on glassware during use. Such defoaming agents are generally used in an amount from about 0.01 to 2%, preferably from about 0.1 to 1% by weight of the compositions.

Minor amounts of other optional additives may be present in the liquid cleaning compositions of the invention if desired. Examples of such additives include perfumes, colorants, opacifying agents, e.g. titanium oxide, dispersing agents, soil suspending agents, fatty acids and hydroxy fatty acids, alkaline salts, anti-tarnish agents and enzymes. It has been found particularly desirable to incorporate in dishwashing compositions an amount of lemon juice which helps provide an attractive fresh smell to the compositions and washed articles, and is associated by the consumer with effective cleaning performance. Such products are also desirably colored yellow by incorporation of a dye or pigment which is resistant to attack by chlorine, for example Direct Yellow 28. The use of this and other yellow dyes is described in U.S. Patent application S/N 348,549 (Rapisarda et al.), which is hereby incorporated by reference. Other colourants for liquid detergent compositions are described in U.S. Patent 4,714,562 (Roselle).

Processing of the compositions of this invention may be done in conventional mixing equipment, but it may be desirable to use a particular order of addition for optimum formulation and dispersion of the ingredients. It is important to disperse any insoluble ingredients such as auxiliary clay thickening agents if they are to be used in translucent products. Generally speaking the presence of air or gas bubbles in the compositions is not desired or necessary, although there are suggestions that the inclusion of very small bubbles can contribute to product stability for liquid dishwashing compositions.

The invention is further illustrated by the following examples which parts and percentages are by weight except as otherwise indicated.

Example 1

A non-phosphate translucent dishwashing detergent composition is made to the following formulation:

Ingredient	%
Water	to 100
Laponite XLS	0.02
Polymeric thickener (Carbopol 940)	1.40
Sodium silicate (Britesil H20)	12.15
Sodium metasilicate	5.00
Sodium polyacrylate (Alcosperse 602-N, 100%)	4.50
Sodium hypochlorite	to 1.00 av Cl
Colourant (Pyrazol Yellow (BG250))	0.004

The composition is prepared by firstly dispensing the Laponite thoroughly in water, and then adding the

Carbopol slowly to the Laponite suspension and mixing until fully dispersed. The sodium metasilicate is then added to neutralize the still acidic Carbopol, after which the Britesil H20 is added to the now strongly alkaline suspension. Alcosperse 602N, which is supplied as a 45% solution, is then mixed in, and finally when the temperature has dropped sufficiently, sodium hypochlorite bleach is added in the form of an aqueous solution, (Sunnysol 150, about 12.5% av Cl) from Jones Chemical company. The yellow colourant is added last after thorough dispersion in some of the water. The pH is about 12.6.

The viscosity of a newly prepared formulation was measured in a Haake Viscometer at 5/sec, and found to have a viscosity of about 5300 cps. After storage at 40 ° C for 13 weeks, the viscosity was found to have increased to nearly about 14000 cps, showing behavior very different from that of conventional phosphate-built compositions, for which the viscosity normally decreases progressively during storage. When a comparative formulation was made using the same Carbopol and Laponite thickener system, but with 19% of tetrapotassium pyrophosphate and 1% tripolyphosphate builder, having an initial viscosity of about 4500 cps, and a pH of 11.8, it is found that the viscosity had decreased to less than 1000 cps, and then to the point when the liquid composition became non-homogeneous, within 2 weeks.

Further tests were undertaken on the chlorine bleach stability for the composition, and it was found that during storage at room temperature, the level of available chlorine fell after 13 weeks storage to about 0.61%, whilst at 40 ° C the available chlorine dropped to about 0.40% after 13 weeks, both of which were acceptable levels at that temperature.

Detergency tests were also done on the formulation of this Example, and the product was found to be effective for spotting and filming performance, as well as overall detergency, with results comparable to commercially available automatic dishwashing products.

The composition was also tested for suitability for dispensing in standard dispenser cups of dishwashing machines. In this test the dispenser cup is filled with a product, then closed, and the dishwashing machines are started on a normal wash cycle, but stopped immediately before the product would otherwise be dispensed. The cup was then opened manually and the amount of product lost from the dispenser cup during the pre-wash and rinse cycles is determined. The amount of the composition of this Example found to be retained in a Kenmore dishwasher dispenser cup was about 83%, and the amount in a Bosch S-512 dispenser cup was about 100%, both of which figures are acceptable compared with current commercial products.

Further products were made to the same formulation except that the polyacrylate (Alcosperse 602N) was replaced by different polymeric polycarboxylate builders as follows:

- A. Sokalan CP-2 (copolymer of methylvinylether/ maleic acid 1:1, MW 70,000)
- B. Sokalan CP-5 (acrylic acid/maleic acid copolymer - 4:1, MW 71,000)
- C. Sokalan PA-30 (acrylic acid homopolymer, MW 8,000)

The products containing these alternative polycarboxylate builder materials were found to have satisfactory viscosity characteristics and washing performance, but the alternative builders were found to be less resistant than Alcosperse to attack by chlorine during storage at 40 ° C and hence could have a shorter shelf life.

Example 2

A low phosphate translucent liquid detergent composition was prepared to the following formulation:

Component	%
Water	to 100
Laponite XLS	0.02
Colourant (Direct Yellow 28)	0.005
Hydrochloric acid	0.007
Polycarboxylate thickener*	2.0
Silicone Antifoam 1400	0.05
Sodium Tripolyphosphate	3.0
Tetrapotassium Pyrophosphate	10.8
Sodium silicate (Britesil H-20)	3.0
Sodium Hydroxide	1.3
Polyacrylate (Alcosperse 602N)	0.45
Hypochlorite	to 1.00 av Cl
Perfume	0.1

* Polyacrylic acid cross-linked with about 2% allyl sucrose, prepared according to U.S. Patent 2,798,053 (MW 10 million).

This composition is prepared by a mixture of the components in essentially the order shown, ensuring that each component is thoroughly admixed before addition of the next, and allowing the mixture to cool before addition of the hypochlorite bleach. The final pH was 12.3.

The product was found in comparative tests to have excellent stability with a shelf-life over 9 months at room temperature, and satisfactory washing performance.

Example 3

A non-phosphate liquid detergent composition was prepared by a procedure similar to that for Example 1, to the following formulation:

Component	%
Water	to 100
Laponite XLS	0.02
Potassium hydroxide	0.5
Polymeric thickener (Carbopol 940)	1.5
Sodium metasilicate	5.0
Sodium silicate (Britesil H20)	12.15
Polyacrylate (Alcosperse 602N, 100%)	4.5
Hypochlorite (Sunnysol 150)	9.48 (about 1.2% av Cl)

This formulation was evaluated for viscosity initially and after storage, with the following results.

Viscosity (cps)				
No. of weeks storage	Room temp (5/sec)	40 ° C (5/sec)	Room temp (21/sec)	40 ° C (21/sec)
0	6111	6111	2203	2203
1	7857	5762	2619	2161
2	7508	13269	2619	2037
3	8905	10301	2951	3118
5	8555	13020	2951	4074
6	13764	-	3986	-
7	8904	-	3035	-
8	8206	-	2910	-
11	11532	11532	3277	3100

These figures demonstrate good thixotropic performance, with retention of satisfactory viscosity over a long period, even under the elevated temperature storage conditions.

In addition, the amount of available chlorine remaining in the composition during storage was determined, and from an initial figure of 0.94% available chlorine, the amount found to remain after 11 weeks storage at room temperature was 0.72% av Cl, and at 40 ° C the amount was 0.48% av Cl.

Claims

1. An aqueous thixotropic liquid detergent composition suitable for automatic dishwashing having improved stability comprising:

- about 0.1 to 5% of a chlorine-releasing bleach agent (calculated as available chlorine),
- about 0.1 to 5% of a cross-linked polycarboxylate thickening agent derived from an unsaturated mono or di-carboxylic acid of 3 to 6 carbon atoms having a molecular weight of at least 1,000,000 and cross-linked by at least about 0.75% of a cross-linking agent based on the monomeric constituents,
- about 1 to 30% of a detergency builder of which at least about 0.25% is an alkali metal or ammonium polymeric polycarboxylate having a molecular weight of from about 1,000 to 100,000,
- about 1 to 30% of an alkaline buffer system comprising an alkali metal silicate or an alkali metal hydroxide or a mixture thereof, to provide a pH of from about 12 to 13.5,

wherein all percentages are by weight of the composition.

2. A composition according to claim 1 wherein the polycarboxylate thickening agent is derived from acrylic or methacrylic acid and is cross-linked by at least 1% of a cross-linking agent based on the monomeric constituents.

3. A composition according to claim 1 wherein the alkali metal silicate is a sodium silicate having a ratio of $\text{SiO}_2:\text{Na}_2\text{O}$ of about 1.6 to 2.2.

4. A composition according to claim 1 wherein the alkali buffer system is sodium or potassium hydroxide or a metasilicate in an amount sufficient to provide a pH of from 12.3 to 13.

5. A composition according to claim 1 which additionally comprises about 0.1 to 10% by weight of a surfactant.

6. A composition according to claim 5 where the surfactant is a nonionic polyoxyalkylene condensation product.

7. A composition according to claim 1 which additionally comprises from about 0.01 to 0.5% by weight of a clay auxiliary thickening agent.

8. A composition according to claim 1 which is essentially free of any phosphate detergency builder.

9. A composition according to claim 1 wherein the polymeric polycarboxylate builder is selected from polyacrylic acid, polymethacrylic acid, polymaleic acid, copolymers of acrylic and maleic acids, and copolymers of vinyl methyl ether and maleic acid, and their salts.

5 10. A composition according to claim 1 which has a viscosity of at least 1000 centipoises at 25 ° C.

11. A composition according to claim 1 wherein the chlorine bleaching agent is sodium hypochlorite.

10 12. A composition according to claim 1 which additionally comprises from about 3 to 20% by weight of a soluble phosphate detergency builder.

13. A composition according to claim 1 wherein said composition is translucent.

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